

Performance of a non-empirical meta-GGA density functional for excitation energies

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It is known that the adiabatic approximation in time-dependent density functional theory usually provides a good description of low-lying excitations of molecules. In the present work, the capability of the adiabatic nonempirical meta-generalized gradient approximation (meta-GGA) of Tao, Perdew, Staroverov, and Scuseria (TPSS) to describe atomic and molecular excitations is tested. The adiabatic (one-parameter) hybrid version of the TPSS meta-GGA and the adiabatic GGA of Perdew, Burke, and Ernzerhof (PBE) are also included in the test. The results are compared to experiments and to two well-established hybrid functionals PBE0 and B3LYP. Calculations show that both adiabatic TPSS and TPSSh functionals produce excitation energies in fairly good agreement with experiments, and improve upon the adiabatic local spin density approximation and, in particular, the adiabatic PBE GGA. This further confirms that TPSS is indeed a reliable nonhybrid universal functional which can serve as the starting point from which higher-level approximations can be constructed. The systematic underestimate of the low-lying vertical excitation energies of molecules with time-dependent density functionals within the adiabatic approximation suggests that further improvement can be made with nonadiabatic corrections.

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I. INTRODUCTION

Density functional theory (DFT) [1, 2, 3] is a mainstream electronic structure theory of many-electron systems, which has achieved a high-level sophistication. While a ladder of highly accurate exchange-correlation (xc) functionals [4, 5, 6] have been constructed, they are essentially not suitable for the description of time-dependent processes and excited states, because these density functionals are only protected by the ground-state Hohenberg-Kohn variational principle. This limitation has been overcome by the most important extension of DFT—time-dependent density functional theory (TDDFT) [7].

In recent years TDDFT has been rapidly grown into a popular method for the investigation of dynamical properties of many-electron systems [8, 9, 10, 11]. It follows the Kohn-Sham strategy and maps the complicated problem of interacting electrons in a time-dependent external potential $v(\mathbf{r}, t)$ to a simpler one of noninteracting electrons moving in a self-consistent time-dependent effective potential $v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + u_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t)$, which generates the density $n(\mathbf{r}, t)$ of the interacting system. Here $u_H(\mathbf{r}, t)$ is the Hartree potential given by $u_H(\mathbf{r}, t) = \int d^3r' n(\mathbf{r}', t)/|\mathbf{r} - \mathbf{r}'|$, and $v_{xc}(\mathbf{r}, t)$ is the dynamical XC potential defined by $v_{xc}(\mathbf{r}, t) \equiv \delta A_{xc}[n]/\delta n(\mathbf{r}, t)$, with $A_{xc}[n]$ being the time-dependent XC functional or XC action, the analogue of the static functional $E_{xc}[n_0]$. In

the linear response, $v_s(\mathbf{r}, t) = v_{s,0}(\mathbf{r}) + v_{s,1}(\mathbf{r}, t)$, where the effective ground-state potential $v_{s,0}(\mathbf{r})$ can be written as the sum of the external potential, the Hartree potential, and the XC potential of the ground state, i.e., $v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + u_{H,0}(\mathbf{r}) + v_{xc,0}(\mathbf{r})$, while the effective perturbation $v_{s,1}(\mathbf{r}, t)$ is the sum of the external (or physical) perturbation, the induced Hartree and XC potentials, $v_{s,1}(\mathbf{r}, t) = v_1(\mathbf{r}, t) + u_{H,1}(\mathbf{r}, t) + v_{xc,1}(\mathbf{r}, t)$.

In TDDFT, the physical excitations can be calculated from the linear response theory [12, 13] through the electron density-density response function [8] $\chi(\mathbf{r}, \mathbf{r}', t, t')$, in which the only unknown part is the XC kernel defined by

$$f_{xc}(\mathbf{r}, \mathbf{r}', t, t') \equiv \frac{\delta v_{xc}([n]; \mathbf{r}, t)}{\delta n(\mathbf{r}', t')}. \quad (1)$$

The key idea is that the exact linear density response of an interacting system to the external perturbation can be written as the linear density response of a noninteracting system to the effective perturbation, i.e.,

$$\begin{aligned} n_1(\mathbf{r}, \omega) &= \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) v_1(\mathbf{r}', \omega) \\ &= \int d\mathbf{r}' \chi_s(\mathbf{r}, \mathbf{r}', \omega) v_{s,1}(\mathbf{r}', \omega), \end{aligned} \quad (2)$$

where

$$\begin{aligned} v_{s,1}(\mathbf{r}, t) &= v_1(\mathbf{r}, t) + \int d\mathbf{r}' \frac{n_1(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \\ &+ \int dt' \int d\mathbf{r}' f_{xc}(\mathbf{r}, \mathbf{r}', t, t') n_1(\mathbf{r}', t), \end{aligned} \quad (3)$$

and $\chi_s(\mathbf{r}, \mathbf{r}', \omega)$ is the Kohn-Sham response function evaluated with the Kohn-Sham ground-state orbitals. For

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spin-unpolarized systems, we have

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = 2 \sum_{j,k} (n_k - n_j) \frac{\phi_k^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - \omega_{jk} + i\delta}, \quad (4)$$

where n_k are the orbital electron occupation numbers. By substituting the effective perturbation $v_{s,1}(\mathbf{r}, t)$ into Eq. (2) with the observation that the poles ω_{jk} of the Kohn-Sham response function are generally different from those of the interacting system, one arrives at an equation [13], from which excitation energies of the interacting system can be calculated as an eigenvalue problem.

As in the static DFT, the dynamical XC potential must be approximated in practice. The simplest construction is the adiabatic approximation [14], which makes use of the ground-state XC potential but replaces the ground-state density $n_0(\mathbf{r})$ with the instantaneous density $n(\mathbf{r}, t)$, namely,

$$v_{xc}^{ad}[n; \mathbf{r}, t] = \left. \frac{\delta E_{xc}[n_0]}{\delta n_0(\mathbf{r})} \right|_{n_0(\mathbf{r})=n(\mathbf{r}, t)}. \quad (5)$$

Within the adiabatic approximation the XC kernel can be calculated from

$$f_{xc}(\mathbf{r}, \mathbf{r}', t, t') \equiv \frac{\delta v_{xc}([n_0]; \mathbf{r})}{\delta n(\mathbf{r}')} \delta(t - t'), \quad (6)$$

which is local in time, while it is not necessarily local in space. This approximation, which completely neglects the vector potential [15, 16, 17] and thus retardation and dissipation effects [18, 19, 20], has been widely used to calculate the single-particle excitation energies [21, 22, 23, 24, 25, 26, 27, 28, 29], although it fails for multi-particle excitations [31, 32] or charge transfer states [33, 34, 35], due to the disregard of the frequency dependence. The detail of the TDDFT linear response theory for the calculation of the excitation energies within the adiabatic approximation has been documented in the literature [12, 13, 21].

Although in general a nonadiabatic correction to the adiabatic approximation is needed even in the low-frequency limit, it has been shown [13, 36] that (at least for small systems) the largest source of error in the prediction of low-lying excitation energies arises from the approximation to the static XC potential. This justifies the adiabatic approximation for the description of low-lying excitations of atoms and molecules. The low-lying excited states in the visible and near-UV region are the most interesting ones. For example, photodissociation often proceeds on the lowest excited potential energy surface, and the photoemission wavelength of materials is controlled by the lowest electronic excitations. A quantitative description of electronic excited states of molecules is important in spectroscopy, photochemistry, and the design of optical materials (e.g., design of dyes). Therefore, assessment of the ability of time-dependent density functionals in describing electronic excitations is of general interest.

In the present work, the capability of the adiabatic nonempirical meta-generalized gradient approximation (meta-GGA) of Tao, Perdew, Staroverov, and Scuseria (TPSS) [5, 37] and its adiabatic one-parameter hybrid version [38] to describe low-lying excitations is tested for eleven atoms with $Z \leq 36$ and prototype small molecules CO, N₂, H₂O, CH₂O (formaldehyde), (CH₃)₂CO (acetone), C₂H₄ (ethylene), C₆H₆ (benzene), and C₅H₅N (pyridine). The reason for choosing these atoms and molecules as our test set is that the high-quality experimental results of these systems are available. The TPSS hybrid functional (TPSSH) [38]

$$E_{xc}^{\text{TPSSH}} = aE_x^{\text{exact}} + (1 - a)E_x^{\text{TPSS}} + E_c^{\text{TPSS}}, \quad (7)$$

contains a global empirical parameter – the exact-exchange mixing coefficient “ $a = 0.1$ ”, which is determined by a fit to experimental atomization energies of molecules. With the introduction of exact exchange, TPSSH functional, however, does not satisfy any universal constraints beyond those satisfied by the TPSS meta-GGA, but it improves the description of the asymptotic behavior of the TPSS potential. This improvement turns out to be helpful in most cases [5].

Since the TPSS meta-GGA is constructed from the GGA of Perdew, Burke, and Ernzerhof (PBE) [4], and PBE GGA is constructed from the local spin density approximation (LSDA), we also include the adiabatic LSDA and the adiabatic PBE GGA in the present test. Then we compare the results to both experiments and two well-established hybrid functionals: PBE0 and B3LYP, former of which is a one-parameter hybrid functional [24] based on the PBE GGA with the choice [39] of 1/4 as its exact-exchange mixing coefficient, and the latter is a three-parameter empirical hybrid functional [40] with 1/5 exact exchange mixed in its exchange component. Numerical results show that both adiabatic TPSS and TPSSH yields low-lying excitation energies of atoms and molecules with fairly good accuracy. In particular, we find that the adiabatic TPSS meta-GGA improves upon the PBE GGA and even the adiabatic LSDA, the latter of which usually works well for molecular excitations. The adiabatic TPSSH consistently yields further improvement and can achieve the comparable accuracy of the most popular hybrid functional B3LYP.

II. COMPUTATIONAL METHOD

All calculations are performed using the GAUSSIAN 03 suite [41]. Vertical excitation energies of molecules are self-consistently calculated using the self-consistent ground-state geometries optimized with respective density functionals and the same basis set as used in the geometry optimization. In order for the test to be reliable, a fairly large basis set should be employed. Since our calculations involve the treatment of both ground state (optimization of molecular geometry) and excited states (with the adiabatic approximation within TDDFT), for

TABLE I: Two lowest-lying singlet excitation energies (in eV) of atoms calculated using six functionals with the basis set 6-311++G(3df,3pd). The mean error (m.e.) (with the sign convention that error = theory - experiment) and the mean absolute error (m.a.e.) are also shown. The mean experimental value of these atoms is 8.06 eV. (1 hartree = 27.21 eV).

Atom	Transition	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
He	1s → 2s	19.59	19.73	20.27	20.58	20.62	20.50	20.62
	1s → 2s	22.99	23.41	24.04	24.23	24.05	23.95	21.22
Li	2s → 2p	1.98	1.98	1.99	1.97	1.95	1.98	1.85
	2s → 3s	3.12	3.09	3.09	3.13	3.23	3.16	3.37
Be	2s → 2p	4.84	4.91	5.06	5.05	4.94	4.88	5.28
	2s → 3s	6.11	6.12	6.29	6.35	6.32	6.21	6.78
Ne	2p → 3s	17.45	17.21	17.55	17.94	18.27	17.88	16.62
	2p → 3p	19.82	19.46	19.74	20.16	20.59	20.11	18.38
Na	3s → 3p	2.25	2.12	2.02	2.02	2.08	2.23	2.10
	3s → 4s	3.05	2.91	2.87	2.90	3.02	3.02	3.19
Mg	3s → 3p	4.24	4.18	4.18	4.19	4.20	4.23	4.35
	3s → 4s	5.02	4.93	5.01	5.06	5.08	5.00	5.39
Ar	3p → 4s	11.32	11.27	11.59	11.81	11.90	11.56	11.55
	3p → 4p	12.68	12.50	12.74	13.00	13.22	12.89	12.91
K	4s → 4p	1.70	1.50	1.36	1.36	1.45	1.64	1.61
	4s → 5s	2.52	2.35	2.28	2.30	2.42	2.43	2.61
Ca	4s → 3d	1.88	1.88	1.87	2.02	2.24	2.16	2.71
	4s → 4p	3.09	2.98	2.90	2.90	2.96	3.03	2.93
Zn	4s → 4p	5.80	5.67	5.59	5.52	5.51	5.65	5.80
	2s → 5s	6.38	6.12	6.10	6.12	6.20	6.22	6.92
Kr	4p → 5s	9.52	9.43	9.72	9.92	10.01	9.69	9.92
	4p → 5p	10.84	10.64	10.85	11.10	11.30	10.98	11.30
m.e.		-0.06	-0.14	-0.02	0.12	0.19	0.09	...
m.a.e.		0.47	0.51	0.49	0.50	0.50	0.47	...

^aFrom Ref. [42].

consistency we chose the same basis 6-311++G(3df,3pd) in all calculations. This large basis set was previously used to perform a comprehensive assessment [38] of the TPSS functional for molecules. The ultrafine grid (Grid=UltraFine) in numerical integration and the tight self-consistent field convergence criterion (SCF=Tight) are used.

To make our comparisons to be consistent, we perform our own calculations with all reference functionals, rather than attempting to extract data from the literature. Throughout the paper, we calculate the mean error (m.e.) (or signed error) using the sign convention: error = theory - experiment. The mean error tells us whether excitation energies are underestimated or overestimated on the average with a particular density functional, while the mean absolute error (m.a.e.) shows us how far a density functional theoretical estimate is from experiment.

III. RESULTS AND DISCUSSIONS

A. Atoms

As a simple test, we present two lowest-lying singlet excitation energies of eleven atoms with $Z \leq 36$: He, Li, Be, Ne, Na, Mg, Ar, K, Ca, Zn, and Kr. They are calculated with the adiabatic LSDA, PBE GGA, PBE0, B3LYP, TPSS meta-GGA, and TPSSh functionals. The

results are shown in Table 1. Experimental values [42] are also listed for comparison.

Table 1 shows that the six adiabatic density functionals tested here produce remarkably accurate excitation energies, all with mean absolute error (m.a.e.) of 0.5 eV. From the mean errors (m.e.), we can see that all nonhybrid functionals (LSD, PBE GGA, and TPSS meta-GGA) slightly underestimate low-lying excitation energies of atoms, while all hybrid functionals (PBE0, B3LYP, and TPSSh) yield overestimates. This suggests the difficulty of further systematic improvement from the nonadiabatic corrections [15, 17]. This is resonant with the numerical studies of atomic excitation energies made by Ullrich and Burke [43].

B. Molecules

Theoretical prediction or interpretation of discrete molecular electronic excitation spectrum is of significant importance. Many physical and chemical properties of materials are directly related to electronic excitations. In this work, we calculate several low-lying excitation energies of our test set, which includes three inorganic (CO, N₂, H₂O) and five organic (CH₂O, (CH₃)₂CO, C₂H₄, benzene, pyridine) molecules. The results are reported in Tables II–IX, respectively.

The performance of the adiabatic LSDA [21, 22, 23,

TABLE II: Low-lying excitation energies (in eV) of CO calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean error (m.e) and the mean absolute error (m.a.e.) are also shown. The mean experimental value is 9.58 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ Π	5.98	5.68	5.75	5.78	5.77	5.89	6.32
³ Σ ⁺	8.45	7.97	7.88	7.88	7.96	8.03	8.51
¹ Π	8.19	8.19	8.40	8.50	8.49	8.47	8.51
³ Δ	9.21	8.59	8.53	8.59	8.70	8.71	9.36
³ Σ ⁻	9.90	9.31	9.64	9.92	9.89	9.80	9.88
¹ Σ ⁻	9.94	9.79	10.05	10.15	9.89	9.86	9.88
¹ Δ	9.90	9.72	9.96	10.01	10.29	10.26	10.23
³ Σ ⁺	9.55	9.72	9.96	10.01	10.05	9.92	10.40
³ Σ ⁺	10.48	10.21	10.60	10.86	10.94	10.85	11.30
¹ Σ ⁺	10.73	10.62	10.89	11.15	11.31	11.32	11.40
m.e.	-0.35	-0.60	-0.41	-0.30	-0.25	-0.28	...
m.a.e.	0.36	0.60	0.45	0.36	0.27	0.28	...

^aFrom Ref. [44].

TABLE III: Low-lying excitation energies (in eV) of N₂ calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 9.38 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ Σ _u ⁺	7.96	7.42	7.22	7.12	7.14	7.25	7.75
³ Π _g	7.62	7.34	7.43	7.54	7.64	7.68	8.04
³ Δ _u	8.90	8.19	8.05	8.01	8.06	8.12	8.88
¹ Π _g	9.11	9.04	9.23	9.37	9.43	9.37	9.31
³ Σ _u ⁻	9.73	9.58	9.82	9.79	9.53	9.47	9.67
¹ Σ _u ⁻	8.73	9.58	9.82	9.79	9.53	9.47	9.92
¹ Δ _u	10.28	9.98	9.95	9.98	10.05	10.86	10.27
³ Π _u	10.39	10.37	10.65	10.79	10.79	10.68	11.19
m.e.	-0.29	-0.44	-0.36	-0.33	-0.36	-0.27	...
m.a.e.	0.36	0.44	0.40	0.38	0.39	0.43	...

^aFrom Ref. [45].

25], PBE GGA [24], PBE0 [24], and B3LYP [21, 22, 23, 24] functionals has been also tested with other bases and discussed elsewhere. In the present work, we shall focus only on the adiabatic TPSS and TPSSh functionals.

Tables II–IV display the vertical excitation energies of three prototype inorganic molecules CO, N₂, and H₂O. For the CO molecule, as shown in Table II, the adiabatic TPSS functional produces the vertical (low-lying) excitation energies in better agreement with the experimental values [44] than the adiabatic PBE GGA, while it is slightly less accurate than the adiabatic LSD. As expected, the adiabatic TPSSh yields further improvement over the TPSS meta-GGA. Partly mixing some amount of the exact exchange into a semilocal functional improves the asymptotic behavior of the XC potential. Similar results are observed for the N₂ molecule, an iso-electron

TABLE IV: Low-lying excitation energies (in eV) of H₂O calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 8.99 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ B ₁	6.30	6.06	6.30	6.59	6.80	6.56	7.14
¹ B ₁	6.60	6.44	6.65	6.96	7.24	6.96	7.49
³ A ₂	7.99	7.72	7.90	8.24	8.57	8.31	9.1
¹ A ₂	8.08	7.88	8.05	8.39	8.77	8.47	9.2
³ A ₁	8.26	8.10	8.36	8.64	8.84	8.58	9.35
¹ A ₁	8.67	8.62	8.86	9.15	9.43	9.10	9.73
³ B ₂	9.94	9.75	9.95	10.26	10.55	10.28	9.93
¹ B ₂	10.14	10.04	10.23	10.57	10.93	10.59	10.0
m.e.	-0.75	-0.92	-0.71	-0.39	-0.10	-0.39	...
m.a.e.	0.78	0.93	0.77	0.62	0.49	0.62	...

^aFrom Ref. [46].

TABLE V: Low-lying excitation energies (in eV) of formaldehyde (H₂CO) calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 6.90 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ A ₂	3.15	3.09	3.26	3.30	3.22	3.26	3.5
¹ A ₂	3.75	3.82	4.06	4.12	4.02	3.99	4.1
³ A ₁	6.37	5.75	5.57	5.46	5.43	5.58	6.0
³ B ₂	5.89	5.68	5.95	6.27	6.53	6.38	7.09
¹ B ₂	5.99	5.89	6.11	6.45	6.77	6.53	7.13
³ B ₂	7.10	6.91	7.17	7.44	7.62	7.46	7.92
¹ B ₂	7.18	7.07	7.29	7.58	7.82	7.61	7.98
³ A ₁	6.86	6.63	6.87	7.21	7.50	7.35	8.11
¹ A ₁	6.95	6.82	7.01	7.36	7.72	7.47	8.14
¹ B ₁	8.86	8.82	9.01	9.15	9.22	9.09	9.0
m.e.	-0.69	-0.87	-0.69	-0.49	-0.31	-0.43	...
m.a.e.	0.77	0.87	0.69	0.52	0.36	0.44	...

^aFrom Refs. [47, 48].

TABLE VI: Low-lying excitation energies (in eV) of acetone ((CH₃)₂CO) calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 6.17 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ A ₂	3.70	3.59	3.69	3.73	3.81	3.81	4.18
¹ A ₂	4.22	4.21	4.37	4.41	4.49	4.44	4.43
³ A ₁	6.13	5.70	5.97	5.96	5.60	5.70	5.88
³ A ₂	6.28	6.11	6.27	6.26	6.01	5.75	6.26
¹ B ₂	5.09	5.00	5.22	5.22	6.08	5.80	6.36
¹ A ₂	6.30	6.14	6.30	6.30	7.18	6.92	7.36
¹ A ₁	6.08	5.92	6.08	6.08	7.02	6.72	7.41
¹ B ₂	6.51	6.36	6.53	6.52	7.37	7.12	7.49
m.e.	-0.63	-0.79	-0.62	-0.61	-0.23	-0.39	...
m.a.e.	0.70	0.79	0.64	0.53	0.24	0.39	...

^aFrom Ref. [24].

TABLE VII: Low-lying excitation energies (in eV) of ethylene (C_2H_4) calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 7.40 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ B _{1u}	4.81	4.26	4.12	4.02	3.97	4.17	4.36
³ B _{3u}	6.75	6.45	6.58	6.74	6.86	6.65	6.98
¹ B _{3u}	6.82	6.58	6.67	6.84	7.01	6.75	7.15
¹ B _{1u}	7.58	7.44	7.53	7.59	7.61	7.48	7.66
³ B _{1g}	6.95	6.99	7.17	7.34	7.39	7.27	7.79
³ B _{2g}	7.34	7.02	7.12	7.31	7.52	7.26	7.79
¹ B _{1g}	7.36	7.16	7.25	7.43	7.60	7.34	7.83
¹ B _{2g}	7.41	7.13	7.21	7.40	7.64	7.34	8.0
³ A _g	8.39	8.03	8.20	8.33	8.37	8.25	8.15
¹ A _g	8.71	8.48	8.56	8.70	8.85	8.63	8.29
m.e.	-0.22	-0.47	-0.37	-0.25	-0.12	-0.29	...
m.a.e.	0.41	0.50	0.42	0.35	0.27	0.37	...

^aFrom Ref. [47].

TABLE VIII: Low-lying excitation energies (in eV) of benzene (C_6H_6) calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 5.89 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ B _{1u}	4.47	3.98	3.84	3.73	3.68	3.84	3.94
³ E _{1u}	4.82	4.61	4.67	4.70	4.75	4.72	4.76
¹ B _{2u}	5.33	5.22	5.32	5.42	5.52	5.41	4.90
³ B _{2u}	5.05	4.89	4.98	5.06	5.12	5.07	5.60
¹ B _{1u}	6.07	5.94	6.00	6.09	6.18	6.05	6.20
¹ E _{1g}	6.12	5.89	5.99	6.18	6.38	6.11	6.33
³ E _{1g}	6.09	5.84	5.95	6.14	6.32	6.07	6.34
¹ A _{2u}	6.70	6.43	6.50	6.69	6.90	6.62	6.93
¹ E _{2u}	6.71	6.44	6.50	6.70	6.95	6.65	6.95
³ E _{1u}	6.66	6.37	6.45	6.63	6.82	6.57	6.98
m.e.	-0.09	-0.33	-0.27	-0.16	-0.03	-0.18	...
m.a.e.	0.30	0.40	0.36	0.26	0.17	0.28	...

^aFrom Ref. [49].

series of the CO molecule. As observed in Table IV, both TPSS and TPSSh functionals describe the vertical excitations of water molecule well and produce the low-lying excitation energies more accurately than the adiabatic LSDA and PBE GGA. As expected, the best results are obtained with the adiabatic hybrid functionals PBE0, B3LYP, and TPSSh. We can see from the mean errors in Tables II–IV that all six adiabatic density functionals tend to underestimate the molecular excitation energies.

Tables V–IX show the low-lying excitation energies of five organic molecules formaldehyde, acetone, ethylene, benzene, and pyridine. The adiabatic TPSS meta-GGA consistently provides a more realistic description of the excitation energies of molecules than the adiabatic PBE GGA, and shows an overall improvement over the adia-

TABLE IX: Low-lying excitation energies (in eV) of pyridine (C_5H_5N) calculated using six functionals with the basis set 6-311++G(3df,3pd). Calculations are performed using the geometry optimized on respective functionals with the same basis. The mean experimental value is 5.07 eV.

Symmetry	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP	Expt ^a
³ B ₁	3.69	3.68	3.84	3.99	3.81	3.97	4.1
³ A ₁	4.59	4.11	3.97	3.86	4.08	4.05	4.1
¹ B ₁	4.22	4.33	4.55	4.74	4.86	4.76	4.59
³ B ₂	4.62	4.41	4.44	4.49	4.54	4.52	4.84
³ A ₁	5.04	4.78	4.81	4.86	4.92	4.88	4.84
¹ B ₂	5.46	5.33	5.41	5.53	5.63	5.52	4.99
³ A ₂	4.19	4.30	4.57	4.83	5.03	4.93	5.40
¹ A ₂	4.29	4.43	4.71	4.99	5.20	5.07	5.43
³ B ₂	5.45	5.40	5.65	6.06	5.72	5.64	6.02*
¹ A ₁	6.03	5.97	6.18	6.31	6.41	6.23	6.38
m.e.	-0.31	-0.40	-0.26	-0.08	-0.05	-0.11	...
m.a.e.	0.54	0.47	0.34	0.25	0.25	0.26	...

^aFrom Ref. [47]; *CASPT2 estimate from Ref. [24, 50].

TABLE X: Mean absolute relative error (m.a.r.e.) of the atoms and molecules listed in Tables I–IX.

	LSD	PBE	TPSS	TPSSh	PBE0	B3LYP
m.a.r.e. (%)	7.3	8.3	7.1	5.7	4.4	5.3

batic LSDA. The adiabatic TPSSh gives further improvement upon the adiabatic TPSS functional, with comparable accuracy of the adiabatic PBE0 and B3LYP functionals. Again as we have already observed in Tables II–IV, these adiabatic density functionals tend to underestimate the vertical excitation energies of molecules.

In order to give an overall order of accuracy for these functionals tested here, we calculate the mean absolute relative errors of these functionals. They are computed as follows. First we calculate the mean experimental value of the excitation energies of the atoms listed in Table I, as given in the caption. We also evaluate the mean experimental value of the excitation energies of each molecule, as shown in the caption of each table. Then we find the relative error of each density functional from the ratio of the mean absolute error to the mean experimental value. Finally we obtain the mean relative error by dividing the sum of the nine mean absolute errors by nine, the number of the mean absolute errors of each functional. In short, the mean absolute relative error is calculated as

$$\text{m.a.r.e} = \frac{\sum[\text{m.a.e.}/\text{mean expt. value of property}]}{\text{number of the mean absolute errors}}. \quad (8)$$

Table X shows the mean absolute relative errors of these functionals. We can see from Table X that the overall order of accuracy for these functionals is

$$\text{PBE} < \text{LSDA} \lesssim \text{TPSS} < \text{TPSSh} \lesssim \text{B3LYP} < \text{PBE0}. \quad (9)$$

The mean absolute relative error of each density functional tested here is less than 10%, suggesting the good

performance of the adiabatic TPSS and TPSSh functionals for the description of low-lying excitations of atoms and molecules.

The systematic underestimate of the low-lying vertical excitation energies of molecules with the adiabatic approximation within TDDFT suggests that further improvement can be made with nonadiabatic corrections, as found by van Faassen et al. [51, 52] with the Vignale-Kohn current-density functional theory [15, 53]. The nonadiabatic corrections for the inhomogeneous system have been recently derived by Tao and Vignale [17, 18].

IV. CONCLUSION

In this work we have tested the ability of the time-dependent density functionals TPSS meta-GGA and TPSSh hybrid within the adiabatic approximation to describe the low-lying excitations of atoms and small molecules. The results show that both density functionals produce the vertical excitation energies in fairly good agreement with experiments and improve upon the adiabatic LSDA and in particular, the adiabatic PBE GGA. This suggests that both TPSS and TPSSh functionals within the simple adiabatic approximation are capable of describing photochemically interesting phenomena when the system is exposed to a time-dependent laser field. Compared to other adiabatic density functionals, the adiabatic TPSS functional yields the best performance among nonhybrid functionals, while the adia-

batic TPSSh functional can achieve the comparable accuracy of the most popular hybrid functionals B3LYP and PBE0. Further comprehensive tests for larger molecular systems [10, 24, 28, 54] are necessary in order to assess performance of these functionals that have been developed for ground-state properties, but not for TDDFT applications to excited states, for new photophysical and photochemical phenomena (such as charge transfer present in nanosystems).

In view of the good performance of the TPSS functional for diverse systems and a wide class of properties, we conclude that TPSS is indeed a reliable nonhybrid universal functional, which can serve as a platform from which higher-level approximations can be constructed. The advantage is that we are able to use the same method and the same basis set to simultaneously describe different class of problems such as chemical reactions on metal surfaces.

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